PCT

(51) International Patent Classification [5]: C08F 4/646	A1	(11) International Publication Number: **WO 94/14856** (43) International Publication Date: 7 July 1994 (07.07.94)

(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US).

(72) Inventors: LO, Frederick, Yip-Kwai; P.O. Box 752, Edison, NJ 08818 (US). NOWLIN, Thomas, Edward; 7 Perrine Path, Cranbury, NJ 08512 (US). SHINOMOTO, Ronald, Steven; 406 Rivendell Way, Edison, NJ 08817 (US). SHIRODKAR, Pradeep, Pandurang; 52 Johnson Road, Somerset, NJ 08873 (US).

(74) Agents: SUNG, Tak, K. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).

(54) Title: A PROCESS FOR FORMING A CARRIER MATERIAL

(57) Abstract

A support containing methylaluminoxane and derivatives thereof is formed by an incipient impregnation of a silica support so that the solution of the aluminoxane fills the pores in the support with no solution left out. The supported aluminoxane eliminates the problem of fluid bed reactor fouling during gas phase polymerization of olefins in the presence of added metallocenes. The fluid bed reactor (10) is a vertical enclosure with a reaction zone (12), comprising a bed of growing polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components, a velocity reduction zone (14), where entrained particles are given opportunity to drop back into the fluidized bed, and a distributor plate (20). The unreacted gas passes through a cyclone separator (22), a filter (24), a compressor (25) and a heat exchanger (26). The distribution plate (20) serves the purpose of diffusing recycle gas through the bed at a rate sufficient to maintain fluidization.

-1-

A PROCESS FOR FORMING A CARRIER MATERIAL

The invention relates to a process for forming a carrier material. The invention is particularly concerned with
5 improvements in low pressure fluid bed gas phase systems for the polymerization and copolymerization of ethylene, undertaken in the presence of catalysts comprising metallocenes of transition metals. The invention aims to eliminate reactor fouling and to maintaining the continuous operation of the distributor plate
10 in the fluid bed gas phase reactor undertaken in the presence of catalysts comprising metallocenes of transition metals.

Polyethylene is produced commercially in a gas phase reaction in the absence of solvents by employing selected chromium and titanium-containing catalysts under specific
15 operating conditions in a fluid bed process. The products of the early production processes exhibited medium-to-broad molecular weight distribution. To be commercially useful in the gas phase fluid bed process, the catalyst must exhibit high activity, with concomittant high catalyst productivity, because
20 gas phase process systems do not include catalyst residue removal procedures. Accordingly, catalyst residue in the polymer product must be so small that it can be left in the polymer without causing any undue problems in the fabrication and/or to the ultimate consumer. To this end, the patent
25 literature is replete with developments of new catalysts, of high activity, with corresponding high productivity values.

The use of metallocene compounds of transition metals as catalysts for polymerization and copolymerization of ethylene is one of those developments. Metallocenes can be described by
30 the empirical formula $Cp_mMA_nB_p$. These compounds in combination with methylalumoxane (MAO) have been used to produce olefin polymers and copolymers, such as ethylene and propylene homopolymers, ethylene-butene and ethylene-hexene copolymers, e.g., see US-A-4542199 and US-A-4404344. Unlike traditional
35 titanium- and vanadium-based Ziegler-Natta catalysts, a metallocene, e.g. a zirconocene catalyst, free of titanium- and vanadium-components produce resins with very narrow molecular

weight distributions (determined as MFR(I_{21}/I_2) of 15 to 18, versus MFR of 25 to 30 for titanium-based catalysts) and with homogeneous short-chain branching distributions.

When traditional titanium-based and vanadium-based
5 catalysts are used to copolymerize ethylene and higher alpha-olefins, the olefin is incorporated in polymer chains nonuniformly, and most of the olefin resides in the shortest polymer chains. With zirconocene catalyst, however, the branching distribution is essentially independent of chain
10 length. LLDPE resins produced with zirconocene catalysts have superior properties. These resins can be used to make films with significantly better clarity and impact strength. Extractables of such resins are lower and the balance of properties in the films between the machine and transverse
15 directions is excellent.

More recently, as exemplified in US-A-5032562, metallocene catalysts containing a second transition metal, such as titanium have been developed which produce bimodal molecular weight distribution products, having a high molecular weight component
20 and a relatively lower molecular weight component. The development of a catalyst which can produce bimodal products in a single reactor is significant per se. That development also provides a commercial alternative to processes which require two reactors to produce bimodal production with production of one
25 of the molecular weight components in a first reactor and transfer of that component to a second reactor and completion of the polymerization with production of the other component of different molecular weight.

Methylalumoxane (MAO) is used as co-catalyst with
30 metallocene catalysts. The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula:
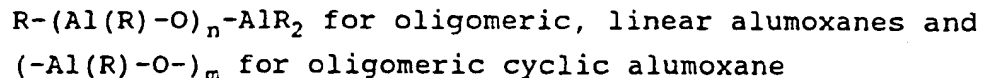
R-(Al(R)-O)$_n$-AlR$_2$ for oligomeric, linear alumoxanes and

(-Al(R)-O-)$_m$ for oligomeric cyclic alumoxane

35 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl.

Methylalumoxane is commonly produced by reacting

-3-

trimethylaluminum with water or with hydrated inorganic salts, such as $CuSO_4 5H_2O$ or $Al_2(SO_4)_3.5H_2O$. Methylalumoxane can be also generated in situ in polymerization reactors by adding to them trimethylaluminum and water or water-containing inorganic salts.

5   MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene. While the MAO solutions remain liquid at fluid bed reactor temperatures, the MAO itself is a solid at room temperature.

10   Most of the experiments reported in the literature relating to methylalumoxane used as a cocatalyst with metallocene catalysts are undertaken in a slurry or solution process, rather than in a gas phase fluid bed reactor process.

          It was found that the metallocene catalyst must contact the
15   MAO cocatalyst while MAO is in solution in order for the catalyst to be activated in the fluid bed reactor. Moreover, it was discovered that extensive reactor fouling results when MAO solutions are fed directly into the gas phase reactor in large enough quantities to provide this liquid contact. The
20   fouling occurs because the MAO solution forms a liquid film on the interior walls of the reactor.

          The catalyst is activated when it comes into contact with this liquid film, and the activated catalyst reacts with ethylene to form a polymer coating which grows larger in size
25   until the reactor is fouled. In addition, since substantially all of the activation takes place on the walls, the MAO is not uniformly distributed to the catalyst particles. The resulting non-homogeneous polymerization gives low catalyst activity and poor product properties.

30   The problems invoked by the use of an alumoxane, particularly methylalumoxane, in catalyst production are addressed by a process for forming a carrier material impregnated with alumoxane and derivatives thereof, comprising

          (1) providing silica which is porous and has a particle
35   size of 1 to 200 microns, having pores which have an average diameter of 50 to 500 Angstroms and having a pore volume of 0.5 to 5.0 cc/g;

-4-

(2) providing a volume of a solution comprising alumoxane of formula (a) or (b)

wherein (a) is $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and (b) is $(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane wherein n is 1-40, m is 3-40, and R is a C_1-C_8 alkyl group and

a solvent for said alumoxane, wherein the volume of solution ranges from less than the pore volume of the silica up to a maximum volume of solution which is equal to the pore volume of the silica, wherein the concentration of alumoxane, expressed as Al weight percent is 5 to 20;

wherein the methylalumoxane provides aluminum in an amount sufficient to provide a molar ratio of Al to silica (wt/wt) from 0.10 to 0.40;

(3) contacting the silica with said volume of said solution and allowing the solution to impregnate the pores of silica, having a pore volume of 0.5 to 5.0 cc/g, containing methylalumoxane within said pores, without forming a slurry of the silica in the solvent;

(4) after said contacting, recovering dry particles of silica impregnated with solid alumoxane.

Advantageously the alumoxane is methylalumoxane.

Preferably the process further comprises heating the dry particles to remove solvent from the pores, under temperature conditions effective to prevent crosslinking of the alumoxane.

Desirably the temperature ranges from above 30°C to below 60°C.

At least one metallocene compound is preferably added to said volume of solution prior to the contcting of step (3), said metallocene being of the formula: $Cp_mMA_nB_p$ wherein

Cp is a cyclopentadienyl or a substituted cyclopentadienyl group;

m is 1 or 2;

M is zirconium or hafnium; and

each of A and B is selected from the group consisting of a halogen atom, a hydrogen atom and an alkyl group, providing that m+n+p is equal to the valence of the metal

-5-

M; wherein the metallocene compound is admixed with an amount of a methylalumoxane effective to activate the metallocene compound to form a catalyst.

The metallocene compound may be selected from the group
5 consisting of bis(cyclopentadienyl)metal dihalides, bis(cyclopenta-dienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides, wherein the halide groups are chlorine and the alkyl
10 groups are C_1- C_6 alkyls.

More preferably the metallocene compound is selected from the group consisting of bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl,
15 bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-
20 butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride

25 It is preferred that the solution has a composition which provides a molar ratio of alumoxane, expressed as aluminum, to metallocene ranging from 50 to 500.

The dry particles preferably exceed a particle size of 1 micron.

30 The dry particles are preferably sieved to isolate dry particles characterized by a particle size of 1-200 microns.

The silica preferably contains reactive hydroxyl groups in an amount ranging from 0.1 to 3.0 mmols/g carrier, and preferably the reactive hydroxyl groups are reacted, prior to
35 said contacting of step (3), with an organomagnesium compound, so that the Mg:OH molar ratio ranges from 0.9:1 to 4:1 wherein the organomagnesium compound has the formula R''_m Mg R'_n

-6-

where R" and R' are the same or different C_2-C_8 alkyl groups, and m and n are each 0, 1 or 2, providing that m + n is equal to the valence of Mg; and, after the reactive hydroxyl groups are reacted but prior to said contacting of step (3), a non-

5 metallocene transition metal is preferably added to the slurry.

Both R" and R' are suitably n-butyl groups.

The non-metallocene compound is preferably a tetravalent titanium compound, which is desirably provided in an amount which is sufficient to provide a metallocene:Ti ratio of 0.01

10 to 0.50.

According to another aspect of the invention there is provided a composition produced by the process as described above.

According to a further aspect of the invention there is

15 provided a fluid bed gas phase reactor process for producing resins, under polymerization conditions effective to form said resins comprising pressures ranging from 100 to 350 psi (690 to 2400 KPa), at temperatures ranging from 30°C to 115°C, in the presence of a catalyst, wherein the catalyst comprises an

20 alumoxane, and wherein the fluidized bed comprises a composition as described above, said process comprising

introducing a feed polymerizable to form said resins; and introducing as cocatalyst a monomeric trialkylaluminum, free of oligomeric or polymeric reaction products of trialkylaluminum

25 and water.

Reference is now made to the accompanying drawings, in which:

Figure 1 is a schematic drawing of a fluid bed reactor for gas phase polymerization of ethylene.

30   Figure 2 is a gel permeation chromatograph of the product of Example 2.

Figure 3 is a gel permeation chromatograph of a bimodal product produced in two reactors.

Figure 4 is a gel permeation chromatograph of the product

35 of Example 4.

Ethylene polymers, as well as copolymers of ethylene with one or more C_3-C_{10} alpha-olefins, can be produced in accordance

-7-

with the invention. Thus, copolymers having two monomeric units
are possible as well as terpolymers having three monomeric
units. Particular examples of such polymers include ethylene/1-
butene copolymers, ethylene/1-hexene copolymers and ethylene/4-
5   methyl-1-pentene copolymers.

Hydrogen may be used as a chain transfer agent in the
polymerization reaction of the present invention. The ratio of
hydrogen/ethylene employed will vary between about 0 to about
2.0 moles of hydrogen per mole of ethylene in the gas phase.
10 Any gas inert to the catalyst and reactants can also be present
in the gas stream.

Ethylene/1-butene and ethylene/1-hexene copolymers are the
most preferred copolymers polymerized in the process of and with
the catalyst of this invention. The ethylene copolymers produced
15 in accordance with the present invention preferably contain at
least about 80 percent by weight of ethylene units. The
cocatalyst of this invention can also be used with the catalyst
precursor of this invention to polymerize propylene and other
alpha-olefins and to copolymerize them. The structure of alpha-
20 olefin polymers prepared with the cocatalyst and the catalyst
precursor of this invention depends on the structure of the
cyclopentadienyl ligands attached to the metal atom in the
catalyst precursor molecule. The cocatalyst compositions of this
invention can also be used with the catalyst precursors of this
25 invention to polymerize cyclo-olefins such as cyclopentene.

In one embodiment, the catalyst used in the invention
exhibits high activity for polymerization of ethylene and higher
alpha-olefins and allows the synthesis of ethylene polymers and
copolymers with a relatively narrow molecular weight
30 distribution and homogeneous branching distribution. The
catalyst used in the invention exhibits high activity for
copolymerization of ethylene and higher alpha-olefins and allows
the synthesis of linear low density polyethylene with a
relatively narrow molecular weight distribution and homogeneous
35 branching distribution. The molecular weight distribution is
determined as MFR which ranges from 15 to 25. Branching
distribution in ethylene copolymers is evaluated on the basis

-8-

of the resin's melting point. Relatively homogeneous branching
distribution is one which the melting point ranges from 100 to
120°C, depending on comonomer composition. In this embodiment,
the catalyst of the invention contains only one source of
5 transition metal, a metallocene.

In another embodiment of the invention, the catalyst of the
invention exhibits high activity for polymerization of ethylene
and higher alpha-olefins and allows the synthesis of ethylene
polymers and copolymers with a broad molecular weight
10 distribution and generally, bimodal molecular weight
distribution with a relatively high molecular weight component
and with a relatively lower molecular weight component in the
resin blend. The molecular weight distribution of the bimodal
resin, expressed as MFR, is about 110 to about 140. In this
15 embodiment, the catalyst of the invention comprises two
transition metal compounds, only one of the transition metal
compounds being a metallocene.

In another embodiment of the invention the catalyst used
in the invention exhibits high activity for copolymerization of
20 ethylene and higher alpha-olefins and allows the synthesis of
linear low density polyethylene with a relatively narrow
molecular weight distribution and homogeneous branching
distribution. The molecular weight distribution is determined
as MFR which ranges from 14 to 24. In this embodiment, the
25 catalyst of the invention contains only one source of transition
metal, a metallocene.

The Fluid Bed Reactor

A fluidized bed reaction system which can be used in the
30 practice of the process according to one aspect of the invention
is shown in Fig. 1. With reference thereto, the reactor 10
consists of a reaction zone 12, a velocity reduction zone 14 and
the distributor plate 20. Although fouling can occur in all of
the cold areas (areas in a reactor at a temperature which is
35 less than the temperature at which any component, in the gas
phase reactor is liquid rather than gaseous) distributor plate
fouling is the one most easily detected, since it results in a

-9-

rapid increase in the pressure drop across the distributor plate
due to flow restriction. Such flow restrictions also result in
changing fluidization patterns and contribute to reactor wall
fouling. The lowest temperature in the reactor loop is in the
5 reactor inlet beneath the distributor plate. Other areas
representing the coldest sections in the fluid bed reactor
system include the cooler and piping between the cooler and the
bottom head.

The reaction zone 12 comprises a bed of growing polymer
10 particles and a minor amount of catalyst particles fluidized by
the continuous flow of polymerizable and modifying gaseous
components. To maintain a viable fluidized bed, the mass gas
flow rate through the bed must be above the minimum flow
required for fluidization, and preferably from about 1.5 to
15 about 10 times G_{mf} and more preferably from about 3 to about 6
times G_{mf}. G_{mf} is used in the accepted form as the abbreviation
for the minimum mass gas flow required to achieve fluidization,
C. Y. Wen and Y. H. Yu, "Mechanics of Fluidization", Chemical
Engineering Progress Symposium Series, Vol. 62, p. 100-111
20 (1966). The distribution plate 20 serves the purpose of
diffusing recycle gas through the bed at a rate sufficient to
maintain fluidization at the base of the bed. Fluidization is
achieved by a high rate of gas recycle to and through the bed,
typically in the order of about 50 times the rate of feed of
25 make-up gas.

Make-up gas is fed to the bed at a rate equal to the rate
at which particulate polymer product is formed by reaction. The
composition of the make-up gas is determined by a gas analyzer
16 positioned above the bed. The composition of the make-up gas
30 is continuously adjusted to maintain an essentially steady state
gaseous composition within the reaction zone.

The portion of the gas stream which does not react in the
bed (the recycle gas) passes a velocity reduction zone 14 where
entrained particles are given an opportunity to drop back into
35 the bed. The unreacted gas stream then passes through a cyclone
22, through a filter 24, through a compressor 25, through a heat
exchanger 26, and is then returned to the bed. The distribution

plate 20 serves the purpose of diffusing recycle gas through the
bed at a rate sufficient to maintain fluidization. The plate
may be a screen, slotted plate, perforated plate, a plate of the
bubble cap type, and the like. The elements of the plate may
5 all be stationary, or the plate may be of the mobile type
disclosed in US-A-3298792.

Conditions in the fluid bed reactor for the gas phase
polymerization and copolymerization of ethylene

10   It is essential to operate the fluid bed reactor at a
temperature below the sintering temperature of the polymer
particles. For the production of ethylene copolymers in the
process of the present invention an operating temperature of
about 30°C to 115°C is preferred, and a temperature of about
15 75°C to 95°C is most preferred. Temperatures of about 75°C to
90°C are used to prepare products having a density of about 0.91
to 0.92, and temperatures of about 80°C to 100°C are used to
prepare products having a density of about 0.92 to 0.94, and
temperatures of about 90°C to 115°C are used to prepare products
20 having a density of about 0.94 to 0.96.

      The fluid bed reactor is operated at pressures of up to
about 1000 psi (6.9 MPa), and is preferably operated at a
pressure of from about 150 to 350 psi (1 Mpa to 2.4 MPa), with
operation at the higher pressures in such ranges favoring heat
25 transfer since an increase in pressure increases the unit volume
heat capacity of the gas.

      The partially or completely activated catalyst is injected
into the bed at a point above the distribution plate at a rate
equal to its consumption. Since the catalysts used in the
30 practice of this invention are highly active, injection of the
fully activated catalyst into the area below the distribution
plate may cause polymerization to begin there and eventually
cause plugging of the distribution plate. Injection into the
bed, instead, aids in distributing the catalyst throughout the
35 bed and precludes the formation of localized spots of high
catalyst concentration.

      The production rate of polymer in the bed is controlled by

-11-

the rate of catalyst injection. Since any change in the rate of catalyst injection changes the rate of generation of the heat of reaction, the temperature of the recycle gas is adjusted to accommodate the change in rate of heat generation. Complete

5 instrumentation of both the fluidized bed and the recycle gas cooling system is, of course, necessary to detect any temperature change in the bed so as to enable the operator to make a suitable adjustment in the temperature of the recycle gas.

10   Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas

15 velocity.

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product.

20

Catalyst Composition

Catalysts which contain only one transition metal in the form of a metallocene have an activity of at least about 3,000 g polymer/g catalyst or about 1,000 kg polymer/g transition

25 metal. Catalysts which contain two transition metals, one in the form of a metallocene and one transition metal in the form of a non-metallocene, have an activity of at least about 2,000 g polymer/g catalyst or about 100 kg polymer/g of transition metals.

30   The catalysts used in the invention comprise a cocatalyst comprising an aluminum alkyl compound, such as a trialkyl aluminum free of alumoxane, and a catalyst precursor comprising a carrier, an alumoxane and at least one metallocene; in one embodiment the catalysts further include a non-metallocene

35 transition metal source.

The carrier material is a solid, particulate, porous, preferably inorganic material, such as an oxide of silicon

-12-

and/or of aluminum. The carrier material is preferably used in
the form of a dry powder having an average particle size of from
about 1 micron to about 250 microns, preferably about 1 to 200
microns, more preferably from about 10 microns to about 150
5 microns. If necessary, the treated carrier material may be
sieved to ensure that the particles of the ultimate carrier-
catalyst containing composition has material is also porous and
has a mesh size of greater than 150 mesh. This is highly
desirable in the embodiment of the invention, in which the
10 catalyst contains only one transition metal in the form of a
metallocene and which is used to form narrow molecular weight
LLDPE, to reduce gels.

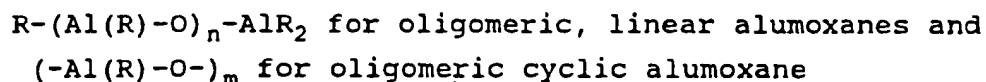The surface area of the carrier may be at least about 3
m^2/g, and preferably is at least about 50 m^2/g up to about 350
15 m^2/g. The carrier material should preferably be dry, that is,
free of absorbed water. Drying of the carrier material can be
effected by heating at about 100°C to about 1000°C, preferably
at about 600°C. When the carrier is silica, it is heated to at
least 200°C, preferably about 200°C to about 850°C and most
20 preferably at about 600°C.

In the most preferred embodiment, the carrier is silica
(with at least some active hydroxyl groups) which, prior to the
use thereof in the first catalyst synthesis step, has been
dehydrated by fluidizing it with nitrogen and heating at about
25 600°C for about 16 hours to achieve a surface hydroxyl group
concentration of about 0.7 millimoles per gram (mmols/g). The
silica of the most preferred embodiment is a high surface area,
amorphous silica (surface area = 300 m^2/g; pore volume of 1.65
cm^3/g), and it is a material marketed under the tradenames of
30 Davison 952 or Davison 955 by the Davison Chemical Division of
W.R. Grace and Company. The silica is in the form of spherical
particles, e.g., as obtained by a spray-drying process.

To form catalysts of the invention, all catalyst precursor
components can be dissolved with alumoxane and impregnated into
35 the carrier. In a unique process, the carrier material is
impregnated with a solid alumoxane, preferably methylalumoxane,
in a process described below. The class of alumoxanes comprises

-13-

oligomeric linear and/or cyclic alkylalumoxanes represented by
the formula:

$R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and

$(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane

5   wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20
and R is a C_1-C_8 alkyl group and preferably methyl. MAO is a
mixture of oligomers with a very wide distribution of molecular
weights and usually with an average molecular weight of about
1200. MAO is typically kept in solution in toluene. While the
10 MAO solutions remain liquid at fluid bed reactor temperatures,
the MAO itself is a solid.

Although the alumoxane can be impregated into the carrier
at any stage of the process of catalyst preparation, the
preferred stage of alumoxane incorporation will depend on the
15 ultimate catalyst sought to be synthesized. The volume of the
solution comprising a solid alumoxane and a solvent therefor can
vary, depending on the catalyst sought to be produced. In a
preferred embodiment, one of the controlling factors in the
alumoxane incorporation into the carrier material catalyst
20 synthesis is the pore volume of the silica. In this preferred
embodiment, the process of impregnating the carrier material is
by infusion of the alumoxane solution, without forming a slurry
of the carrier material, such as silica, in the alumoxane
solution. The volume of the solution of the alumoxane is
25 sufficient to fill the pores of the carrier material without
forming a slurry in which the volume of the solution exceeds the
pore volume of the silica; accordingly and preferably, the
maximum volume of the alumoxane solution is, does not exceed,
the total pore volume of the carrier material sample. That
30 maximum volume of the alumoxane solution ensures that no slurry
of silica is formed.

Accordingly, if the pore volume of the carrier material is
1.65 cm^3/g, then the volume of alumoxane will be equal to or
less than 1.65 cm^3/g of carrier material. As a result of this
35 proviso, the impregnated carrier material will appear dry
immediatedly following impregnation although the pores of the
carrier will be filled with inter alia solvent.

-14-

Solvent may be removed from the alumoxane impregnated pores
of the carrier material by heating and/or under a positive
pressure induced by an inert gas, such as nitrogen. If
employed, the conditions in this step are controlled to reduce,
5 if not to eliminate, agglomeration of impregnated carrier
particles and/or crosslinking of the alumoxane. In this step,
solvent can be removed by evaporation effected at relatively low
elevated temperatures of above about 40°C and below about 50°C
to obviate agglomeration of catalyst particles and crosslinking
10 of the alumoxane. Although solvent can be removed by
evaporation at relatively higher temperatures than that defined
by the range above about 40°C and below about 50°C, very short
heating times schedules must be employed to obviate
agglomeration of catalyst particles and crosslinking of the
15 alumoxane.

In a preferred embodiment, the metallocene is added to the
solution of the alumoxane prior to impregnating the carrier with
the solution. Again the maximum volume of the alumoxane
solution also including the metallocene is the total pore volume
20 of the carrier material sample. The mole ratio of alumoxane
provided aluminum, expressed as Al, to metallocene metal
expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75
to 300, and most preferably 100 to 200. An added advantage of
the present invention is that this Al:Zr ratio can be directly
25 controlled. In a preferred embodiment the alumoxane and
metallocene compound are mixed together at a temperature of
about 20°C to 80°C, for 0.1 to 6.0 hours, prior to use in the
infusion step. The solvent for the metallocene and alumoxane
can be appropriate solvents, such as aromatic hydrocarbons,
30 halogenated aromatic hydrocarbons, ethers, cyclic ethers or
esters, preferably it is toluene.

The metallocene compound has the formula $Cp_mMA_nB_p$ in which
Cp is an unsubstituted or substituted cyclopentadienyl group,
M is zirconium or hafnium and A and B belong to the group
35 including a halogen atom, hydrogen or an alkyl group. In the
above formula of the metallocene compound, the preferred
transition metal atom M is zirconium. In the above formula of

the metallocene compound, the Cp group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group may be straight-chain C_1-C_6 alkyl groups. The cyclopentadienyl group may also be a

5 part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when m in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups

10 can be also bridged by polymethylene or dialkylsilane groups, such as -CH_2-, -CH_2-CH_2-, -CR_1R_2- and -CR_1R_2-CR_1R_2- where R_1 and R_2 are short alkyl groups or hydrogen, -$Si(CH_3)_2$-, $Si(CH_3)_2$-CH_2-CH_2-$Si(CH_3)_2$- and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound

15 are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine. If the substituents A and B in the above formula of the metallocene compound are alkyl groups, they are preferably straight-chain or branched C_1-C_8 alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl,

20 n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and

25 bis(indenyl)metal dihalides wherein the metal is zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C_1-C_6 alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride,

30 bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride, bis(pentamethylcyclopentadienyl)zirconium dichloride,

35 bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride,

-16-

bis(4,5,6,7-tetrahydro-1-indenyl)zirconium   dichloride,   and
ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)]   zirconium
dichloride.

The metallocene compounds utilized within the embodiment
5 of this art can be used as crystalline solids, as solutions in
aromatic hydrocarbons or in a supported form.

As stated above, the alumoxane can be impregnated into the
carrier at any stage of the process of catalyst preparation.
When the catalyst contains two transition metals components, one
10 of which is a metallocene, and one of which is non-metallocene
(free of unsubstituted or substituted cyclopentadienyl groups)
the impregnation of the alumoxane in accordance with the unique
method described above is preferably undertaken after hydroxyl
groups of the carrier material are reacted with an
15 organomagnesium compound and the non-metallocene transition
metal compound. In this embodiment, the amount of Al, provided
by alumoxane, is sufficient to provide an Al:transition metal
(provided by metallocene) mole ratio ranging from 50 to 500,
preferably 100 to 300. The carrier material, having said (OH)
20 groups, is slurried in a non-polar solvent and the resulting
slurry is contacted with at least one organomagnesium
composition having the empirical formula below. The slurry of
the carrier material in the solvent is prepared by introducing
the carrier into the solvent, preferably while stirring, and
25 heating the mixture to about 25°C to about 70°C, preferably to
about 40°C to about 60°C. Temperatures here are critical with
respect to the non-metallocene transition metal which is
subsequently added; that is temperatures in this slurry of about
90°C result in deactivation of the transition metal added
30 subsequently.   The slurry is then contacted with the
aforementioned organomagnesium composition, while the heating
is continued at the aforementioned temperature.

The organomagnesium composition has the empirical formula

$$R''_m \, Mg \, R'_n$$

35 where R" and R' are the same or different C_2-C_{12} alkyl groups,
preferably C_4-C_{10} alkyl groups, more preferably C_4-C_8 normal
alkyl groups, and most preferably both R" and R' are n-butyl

groups, and m and n are each 0, 1 or 2, providing that m + n is equal to the valence of Mg.

Suitable non-polar solvents are materials in which all of the reactants used herein, i.e., the organomagnesium
5 composition, and the transition metal compound, are at least partially soluble and which are liquid at reaction temperatures. Preferred non-polar solvents are alkanes, such as hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane,
10 aromatics, such as benzene, toluene and ethylbenzene, may also be employed. The most preferred non-polar solvent is cyclopentane. Prior to use, the non-polar solvent should be purified, such as by percolation through silica gel and/or molecular sieves, to remove traces of water, oxygen, polar
15 compounds, and other materials capable of adversely affecting catalyst activity.

In the most preferred embodiment of the synthesis of this catalyst it is important to add only such an amount of the organomagnesium composition that will be deposited - physically
20 or chemically - onto the support since any excess of the organomagnesium composition in the solution may react with other synthesis chemicals and precipitate outside of the support. The carrier drying temperature affects the number of sites on the carrier available for the organomagnesium composition - the
25 higher the drying temperature the lower the number of sites. Thus, the exact molar ratio of the organomagnesium composition to the hydroxyl groups on the carrier will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium composition is added to the solution as
30 will be deposited onto the support without leaving any excess of the organomagnesium composition in the solution.

Furthermore, it is believed that the molar amount of the organomagnesium composition deposited onto the support is greater than the molar content of the hydroxyl groups on the
35 support. Thus, the molar ratios given below, are intended only as an approximate guideline and the exact amount of the organomagnesium composition in this embodiment must be

controlled by the functional limitation discussed above, i.e.,
it must not be greater than that which can be deposited onto the
support. If greater than that amount is added to the solvent,
the excess may react with the non-metallocene transition metal
5 compound, thereby forming a precipitate outside of the support
which is detrimental in the synthesis of our catalyst and must
be avoided. The amount of the organomagnesium composition which
is not greater than that deposited onto the support can be
determined in any conventional manner, e.g., by adding the
10 organomagnesium composition to the slurry of the carrier in the
solvent, while stirring the slurry, until the organomagnesium
composition is detected as a solution in the solvent.

For example, for the silica carrier heated at about 600°C,
the amount of the organomagnesium composition added to the
15 slurry is such that the molar ratio of Mg to the hydroxyl groups
(OH) on the solid carrier is about 0.5:1 to about 4:1,
preferably about 0.8:1 to about 3:1, more preferably about 0.9:1
to about 2:1 and most preferably about 1:1. The organomagnesium
composition dissolves in the non-polar solvent to form a
20 solution from which the organomagnesium composition is deposited
onto the carrier.

It is also possible to add such an amount of the
organomagesium composition which is in excess of that which will
be deposited onto the support, and then remove, e.g., by
25 filtration and washing, any excess of the organomagnesium
composition. However, this alternative is less desirable than
the most preferred embodiment described above.

After the addition of the organomagnesium composition to
the slurry is completed, the slurry is contacted with a non-
30 metallocene transition metal compound, free of substituted or
unsubstituted cyclopentadienyl groups. The slurry temperature
must be maintained at about 25°C to about 70°C, preferably to
about 40°C to about 60°C. As noted above, temperatures in this
slurry of about 80°C or greater result in deactivation of the
35 non-metallocene transition metal. Suitable non-metallocene
transition metal compounds used herein are compounds of metals
of Groups IVA, and VA, of the Periodic Chart of the Elements,

-19-

as published by the Fisher Scientific Company, Catalog No. 5-
702-10, 1978, providing that such compounds are soluble in the
non-polar solvents. Non-limiting examples of such compounds are
titanium and vanadium halides, e.g., titanium tetrachloride,
5 $TiCl_4$, vanadium tetrachloride, VCl_4, vanadium oxytrichloride,
$VOCl_3$, titanium and vanadium alkoxides, wherein the alkoxide
moiety has a branched or unbranched alkyl radical of 1 to about
20 carbon atoms, preferably 1 to about 6 carbon atoms. The
preferred transition metal compounds are titanium compounds,
10 preferably tetravalent titanium compounds. The most preferred
titanium compound is titanium tetrachloride. The amount of
titanium or vanadium, in non-metallocene form ranges from a
Ti/Mg molar ratio of 0.5 to 2.0, preferably from 0.75 to 1.50.

Mixtures of such non-metallocene transition metal compounds
15 may also be used and generally no restrictions are imposed on
the transition metal compounds which may be included. Any
transition metal compound that may be used alone may also be
used in conjunction with other transition metal compounds.

Incorporation of the alumoxane-metallocene can be directly
20 to this slurry. Alternatively, and in accordance with the
unique method of infusion of alumoxane into the pores of the
carrier, descibed above, the carrier slurry can be stripped of
solvent, after the addition of the non-metallocene transition
metal compound, to form a free-flowing powder. The free flowing
25 powder can then be impregnated by determining the pore volume
of the carrier and providing an alumoxane (or metallocene-
alumoxane) solution in a volume equal to or less than that of
the pore volume of the carrier, and recovering a dry catalyst
precursor. The resulting free-flowing powder, referred to
30 herein as a catalyst precursor, is combined with an activator
(sometimes referred as a cocatalyst). The cocatalyst can be a
trialkylaluminum, free of alumoxane. Preferably,
trimethylaluminum (TMA) is the cocatalyst or activator. The
amount of the TMA activator is sufficient to give an Al:Ti molar
35 ratio of about 10:1 to about 1000:1, preferably about 15:1 to
about 300:1, and most preferably about 20:1 to about 100:1. The
catalyst exhibits high activity for long periods of time in the

-20-

pilot plant, and exhibits little deactivation.

The catalyst precursor of this invention comprises a metallocene compound and an alumoxane which is fed to the fluid bed reactor for gas phase polymerizations and copolymerizations
5 of ethylene in particulate form. The cocatalyst or activator is fed to the fluid bed reactor for polymerizations and copolymerizations of ethylene in the absence of alumoxane solution.

The invention will now be exemplified by way of the
10 following examples.

Example 1

The titanium component of the catalyst was prepared using a chemical impregnation technique. The zirconium component of
15 the catalyst was prepared using a physical impregnation method. Solution (A): To a 50 ml serum-bottle 0.140 grams of Cp_2ZrCl_2 was transferred and then 10.2 grams of a methylalumoxane (13.2 wt. % Al) solution were added. The solution remained at room temperature for 60 minutes until the entire contents were
20 transferred to the silica slurry described below.

Into a 100ml pear-flask equipped with a magnetic stirring bar, 3.0 grams of Davison 955 silica calcined at 600°C, was added followed by addition of about 20 ml. dry toluene. The flask was placed into a 59°C oil bath. Next, 2.9 ml. of
25 dibutylmagnesium (0.74 mmol/ml) was added to the silica/toluene slurry. The contents of the flask were stirred for 25 minutes. Then, 2.3 mls of a 0.94 molar titanium tetrachloride solution in heptane was added to the flask. The slurry turned a dark brown color and stirring was continued for 25 minutes. Finally,
30 the entire contents of solution (A) was transferred into the catalyst preparation flask, and the slurry was allowed to stir for 10 minutes. After this time, all solvents were removed by evaporation under a nitrogen purge. Catalyst yield was 5.6 grams of a dark-brown free-flowing powder. The Al/Zr ratio was
35 104.

-21-

Example 2

Ethylene/1-hexene copolymer was prepared with the catalyst of the foregoing example under polymerization conditions to produce high density polyethylene (HDPE), with a flow index
5 (I_{21}) of about 6.

A 1.6 liter stainless steel autoclave, at about 50°C, was filled with 0.750 liters of dry heptane, 0.030 liters of dry 1-hexene and 4.0 mmols of trimethylaluminum (TMA) while under a slow nitrogen purge. The reactor was closed, the stirring rate
10 was set at about 900 rpm, the internal temperature was increased to 85°C, and the internal pressure was raised from 7 psi to 10 psi (48 KPa to 69 KPa) with hydrogen. Ethylene was introduced to maintain the reactor pressure at about 203 psi (1.4 MPa). Next, 0.0639 grams of catalyst was introduced into the reactor
15 with ethylene over pressure and the temperature was increased and held at 95°C. The polymerization was continued for 60 minutes, and then the ethylene supply was stopped and the reactor allowed to cool to room temperature. 78 grams of polyethylene were collected.
20   The molecular weight distribution (MWD) of the polymer was examined by Gel Permeation Chromatography (GPC), and the results clearly show that the polymer has a bimodal MWD (Figure 2). Figure 3 shows the GPC chromatogram for a HDPE polymer prepared in tandem gas phase reactor. Comparison of the two GPC
25 chromatograms clearly shows that the polymer prepared in a single reactor is essentially the same as the polymer prepared in two tandem reactors.

Presently, commercial samples of HDPE with a bimodal MWD are produced in a tandem reactor process. In that process, two
30 reactors are run in series and the catalyst is exposed to ethylene polymerization conditions in one reactor, and the resulting polymer-catalyst particles are transferred to a second reactor for additional polymerization. One of the main process differences in the two different reactors, is that the amount
35 of hydrogen is different in the two different reactors. Relatively lower molecular weight product is produced in the reactor containing more hydrogen, because the hydrogen acts as

-22-

a chain transfer agent; whereas relatively higher molecular
weight product is produced in the reactor containing lesser
relative amounts of hydrogen.

5   Example 3

        This catalyst was prepared in two stages. 495 grams of
Davison grade 955 silica, previously calcined with dry nitrogen
for about 12 hours at 600°C, was added to a 2 gallon stainless
steel autoclave under a slow nitrogen purge to eliminate oxygen
10 and moisture from the catalyst preparation vessel. Then, 4.0
liters of dry isopentane (IC5) was added to the autoclave and
the silica/IC5 were slurried at about 100 rpm and the internal
temperature was maintained at about 55-60°C. Next, 469 ml of
a 0.76 molar solution of dibutylmagnesium in heptane was added
15 to the silica/IC5 slurry and stirring was continued for 60
minutes. Next, 39.1 ml of neat titanium tetrachloride was
diluted with about 40 ml of IC5 and this solution was added to
the autoclave and stirring was continued for 60 minutes.
Finally, the solvents were removed with a nitrogen purge through
20 a vent line and 497 grams of a brown free-flowing powder were
obtained. Ti found was 2.62 wt%; Mg found was 1.33 wt% and
Ti/Mg molar ratio was 1.0.

        492 grams of the product of the first stage was added to
a 1.6 gallon glass catalyst preparation vessel fitted with a
25 temperature jacket and an internal stirrer. The product of the
first stage had an estimated pore volume of 1.5 cm^3/g (i.e. 738
cm^3 of pore volume). Then into a stainless steel Hoke bomb was
added 13.93 grams of $(BuCp)_2ZrCl_2$ (34.4 mmol Zr) and 717.5 ml of
a methylalumoxane solution (3,444 mmol of Al) in toluene (4.8
30 Molar). Note: The total volume of the methylalumoxane/toluene
solution is equal to or less than the total pore volume of the
product of the first step. Next, the toluene solution
containing the methylalumoxane and the zirconium compound were
mixed and then the solution was added to the product of the
35 first step in approximately 5 ml aliquots over 90 minutes;
(during this time, the product of the first step remains
completely dry and always consists of a free-flowing powder).

-23-

Finally, nitrogen is purged through the glass vessel for about 5 hours with the jacket temperature at about 45°C. Yield: 877 grams of a free-flowing powder. Ti found was 1.85 wt%; Zr found was 0.30 wt%.

5

Example 4

The catalyst described in Example 3 was examined in a pilot plant fluid bed gas phase reactor under the following conditions:

ethylene	180 psi (1.2 Mpa)
hydrogen/ethylene	0.005-0.008
hexene/ethylene	0.015
reactor temperature	95°C

The resin prepared at a productivity of about 1400 g polymer/g catalyst had the following characteristics:

average particle size	0.017 inches (0.43 mm)
resin metal content	13.0 ppm
HLMI (I21)	5.3
MFR (I21/I2.16)	113
Density	0.949 g/cm^3

The GPC curve of this product is in Figure 4 [solid line] and is compared to a commercially produced tandem unit in a two stage process, in which a different molecular weight component is made in each stage [dotted line in Figure 4.]

Properties of films of the product of Example 4 [solid line in Figure 4] are compared to the commercially produced product [dotted line in Fig. 4] OxyChem L5005.

-24-

Sample	Ti/Zr	OxyChem L5005
I_{21}	5.3	8.0
MFR	113	160
5 Density	0.949	0.950
Throughput, lb/hr (kg/hr)	98 (44)	120 (54)
Melt Pressure (at 120 lb/hr) psi	7550	6450
(MPa)	(52)	(44)
FQR	15	15
10 Dart Drop, 1 mil.g	565	325
0.5 mil.g	410	420
MD Elmendorf Tear, 0.5 mil. g/mil	37	25

15   The results in the GPC curve of Figure 4 show that the
Example 4 bimodal product [solid line] has a high molecular
weight component with higher molecular weight than that produced
in the tandem two reactor process. The film of Example 4 is
substantially reduced in, if not free of, gel content. The film
20 of the Example 4 product has improved dart impact.

Comparative Example 1

      A zirconium catalyst was tested in a slurry reactor at 85°C
with 130 psi (900 KPa) ethylene partial pressure.   A
25 hexene/ethylene gas ratio of 0.03 was used.   MAO/toluene
solution (12 wt.%, 2 ml) was added to the reactor. Productivity
of 800 g resin/g catalyst/hr was measured.

      The same catalyst system was tested in the fluid bed
reactor at 90°C with 200 psi (1.4 MPa) ethylene partial
30 pressure. A 0.025 hexene to ethylene gas ratio was used. A
feed rate of 150 to 200 cm^3/hr of 2 wt% MAO/toluene solution was
employed.   The MAO solution was added below the distributor
plate.   Even at very high MAO/toluene feed rates, catalyst
productivity was only 220 g resin/g catalyst/hr. In addition,
35 the reactor had to be shut down due to a fouled plate only 18
hours after the MAO feed was started.

      This example illustrates that it is more effective to

-25-

activate zirconium catalysts prior to introduction into a gas
phase reactor.   It also illustrates the fouling problems
experienced when MAO solutions are added to the gas-phase
reactor.

5

Comparative Example 2

        A titanium/zirconium mixed metal catalyst was tested in the
fluid bed reactor. At 150 psi (1 MPa) ethylene partial pressure
at 90°C a 0.04 hexene to ethylene gas ratio was employed, and
10 a hydrogen to ethylene gas ratio was 0.045 . A 2 wt% solution
of MAO in toluene was added beneath the fluid bed distributor
plate. Resin flow index and GPC curve analysis showed that the
zirconium catalyst sites were active, and the Ti:Zr productivity
ratio was 7:3. However, the reactor had to be shut down within
15 24 hours because the distributor plate had fouled.

Comparative Example 3

        The same titanium/zirconium catalyst used in Example 2 was
tested in the fluid bed reactor. It was run at 90°C with 150
20 psi (1 MPa) ethylene partial pressure.   A 0.03 hexene to
ethylene gas ratio was used and a hydrogen to ethylene ratio was
0.04 . A solution of 2 wt% MAO in toluene was added directly
into the bed at the rate of 200 cc/hr. The resin flow index and
molecular weight distribution showed definitively that the
25 zirconium sites were active with a Ti:Zr productivity ratio of
3:7. In the process of running this test, though, a very large
chunk grew around the injection port causing a shutdown.
        This example demonstrates that relative zirconocene
catalyst activity is significantly higher when there is better
30 contact between the MAO/toluene droplets and the catalyst sites.
It also verifies that fouling also occurs when the MAO solution
is added to the reactor directly into the fluid-bed of polymer.

Comparative Example 4

35   The catalyst used in examples 2 and 3 was re-run under the
same conditions used in example 3. The MAO feed rate was the
same as well. During this test, though, the MAO was dispersed

into a 10 lb/hr (4.5 Kg/hr) ethylene gas stream using an
ultrasonic atomizer. The atomizer dispersed the MAO solution
into very small (40 micron) droplets.

Enough gas was used so that the toluene evaporated from the
5 MAO. The gas flow rate was determined in an off-line test using
toluene alone. The resin produced during this test showed no
evidence of activity from the zirconium sites. In addition,
there were no signs of reactor fouling after an extended period
of running.

10 This example proves that it is the presence of liquid in
the reactor that is responsible both for the activation of the
zirconium and the fouling of the reactor.

-27-

Claims

1.   A process for forming a carrier material impregnated with
alumoxane and derivatives thereof comprising

5   (1) providing silica which is porous and has a particle
size of 1 to 200 microns, having pores which have an average
diameter of 50 to 500 Angstroms and having a pore volume of 0.5
to 5.0 cc/g;

         (2) providing a volume of a solution comprising alumoxane
10 of formula (a) or (b)
                    wherein (a) is $R-(Al(R)-O)_n-AlR_2$ for oligomeric,
                    linear alumoxanes and (b) is $(-Al(R)-O-)_m$ for
                    oligomeric cyclic alumoxane wherein n is 1-40,   m is
                    3-40,   and R is a C_1-C_8 alkyl group and

15 a solvent for said alumoxane, wherein the volume of solution
ranges from less than the pore volume of the silica up to a
maximum volume of solution which is equal to the pore volume of
the silica, wherein the concentration of alumoxane, expressed
as Al weight percent is 5 to 20;

20   wherein the methylalumoxane provides aluminum in an amount
sufficient to provide a molar ratio of Al to silica (wt/wt) from
0.10 to 0.40;

         (3) contacting the silica with said volume of said solution
and allowing the solution to impregnate the pores of silica,
25 having a pore volume of 0.5 to 5.0 cc/g, containing
methylalumoxane within said pores, without forming a slurry of
the silica in the solvent;

         (4) after said contacting, recovering dry particles of
silica impregnated with solid alumoxane.

30 2.   A process according to Claim 1, wherein the alumoxane is
methylalumoxane.

3.   A process according to Claim 1, which further comprises
heating the dry particles to remove solvent from the pores,
under temperature conditions effective to prevent crosslinking
35 of the alumoxane.

4.   A process according to Claim 3, wherein the temperature
ranges from above 30°C to below 60°C.

-28-

5.   A process according to Claim 1, which further comprises adding, to said volume of solution prior to said contacting, at least one metallocene compound of the formula: $Cp_m MA_n B_p$ wherein

5   Cp is a cyclopentadienyl or a substituted cyclopentadienyl group;

m is 1 or 2;

M is zirconium or hafnium; and

each of A and B is selected from the group consisting of a halogen atom, a hydrogen atom and an alkyl group,

10   providing that m+n+p is equal to the valence of the metal M; wherein the metallocene compound is admixed with an amount of a methylalumoxane effective to activate the metallocene compound to form a catalyst.

6.   A process according to Claim 5, wherein the metallocene

15 compound is selected from the group consisting of bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides, wherein the halide groups are

20 chlorine and the alkyl groups are C_1- C_6 alkyls.

7.   A process according to Claim 6, wherein the metallocene compound is selected from the group consisting of bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride,

25 bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride, bis(pentamethylcyclopentadienyl)zirconium dichloride,

30 bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium

35 dichloride

8.   A process according to Claim 7, wherein the solution has a composition which provides a molar ratio of alumoxane,

expressed as aluminum, to metallocene ranging from 50 to 500.

9.   A process according to Claim 1, wherein the dry particles exceed a particle size of 1 micron.

10.   A process according to Claim 11, which further comprises
5 sieving the dry particles to isolate dry particles characterized by a particle size of 1-200 microns.

11.   A process according to Claim 1, wherein the silica contains reactive hydroxyl groups in an amount ranging from 0.1 to 3.0 mmols/g carrier, and wherein the reactive hydroxyl groups are
10 reacted, prior to said contacting of step (3), with an organomagnesium compound, so that the Mg:OH molar ratio ranges from 0.9:1 to 4:1 wherein the organomagnesium compound has the formula $R''_m Mg R'_n$

where R'' and R' are the same or different C_2-C_8 alkyl groups,
15 and m and n are each 0, 1 or 2, providing that $m + n$ is equal to the valence of Mg; and, after the reactive hydroxyl groups are reacted but prior to said contacting of step (3), adding a non-metallocene transition metal to the slurry.

12.   A process according to Claim 11, wherein both R'' and R' are
20 n-butyl groups.

13.   A process according to Claim 11, wherein the non-metallocene compound is a tetravalent titanium compound.

14.   A process according to Claim 13, wherein the tetravalent titanium compound is provided in an amount which is sufficient
25 to provide a metallocene:Ti ratio of 0.01 to 0.50.

15.   A composition produced by the process of claim 1.

16.   A fluid bed gas phase reactor process for producing resins, under polymerization conditions effective to form said resins comprising pressures ranging from 100 to 350 psi (690 to 2400
30 KPa), at temperatures ranging from 30°C to 115°C, in the presence of a catalyst, wherein the catalyst comprises an alumoxane, and wherein the fluidized bed comprises a composition according to claim 15, said process comprising

introducing a feed polymerizable to form said resins; and
35 introducing as cocatalyst a monomeric trialkylaluminum, free of oligomeric or polymeric reaction products of trialkylaluminum and water.
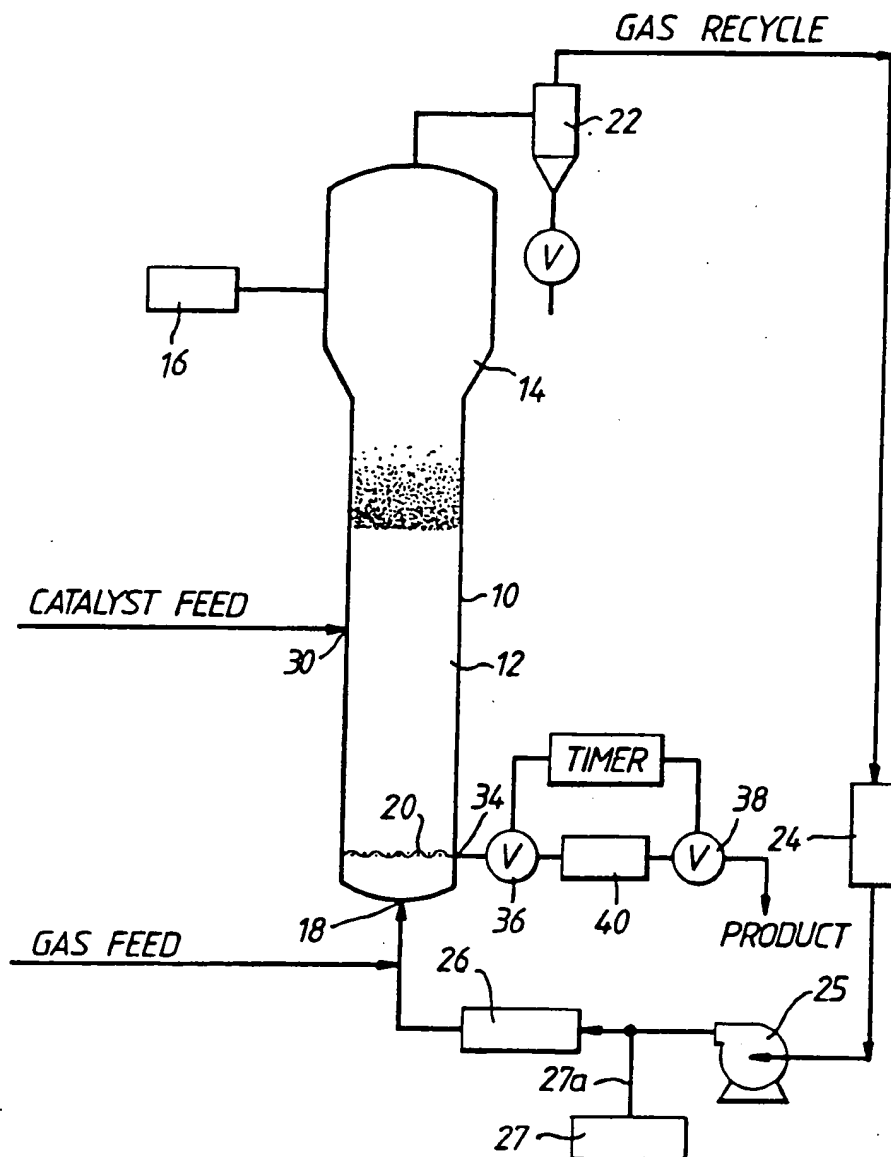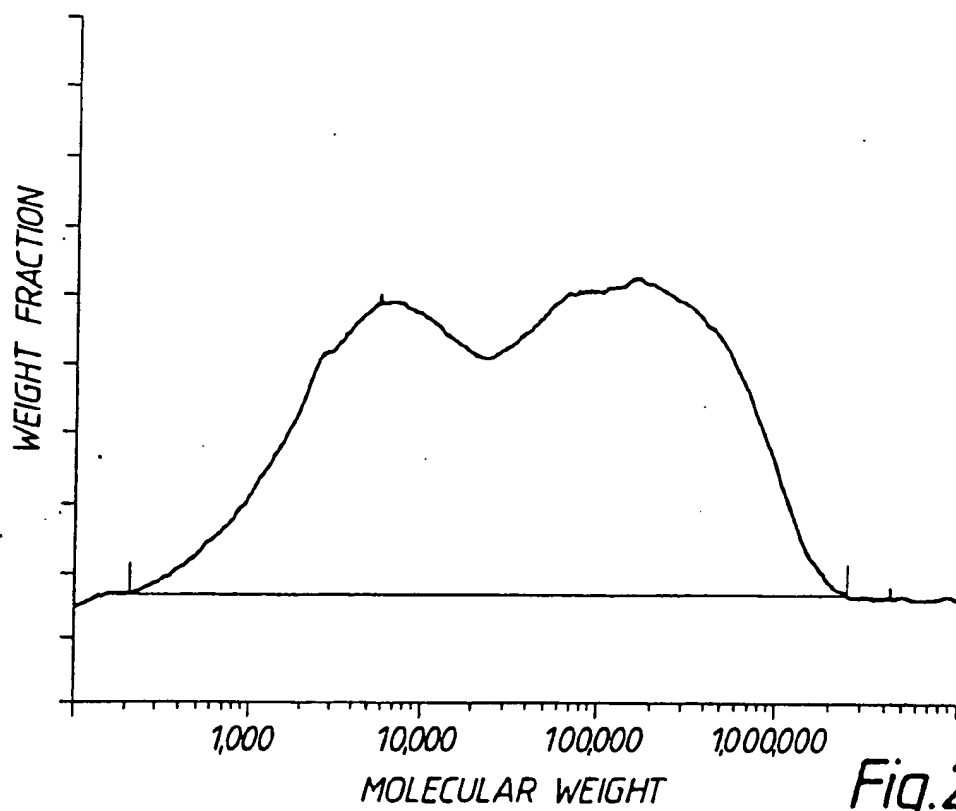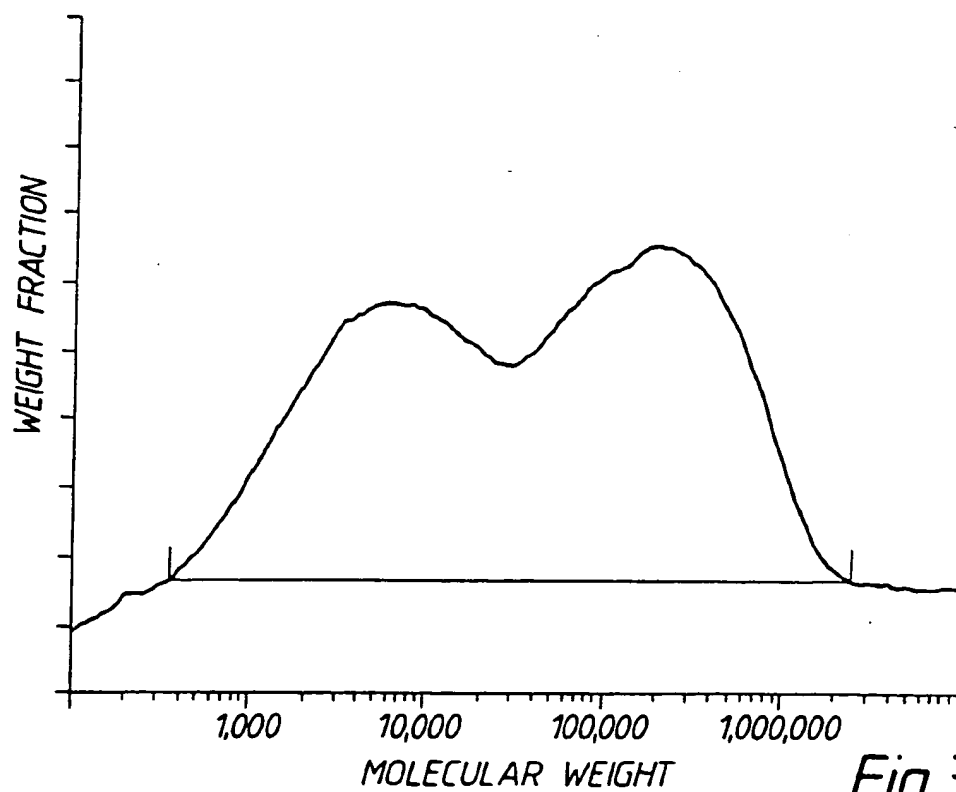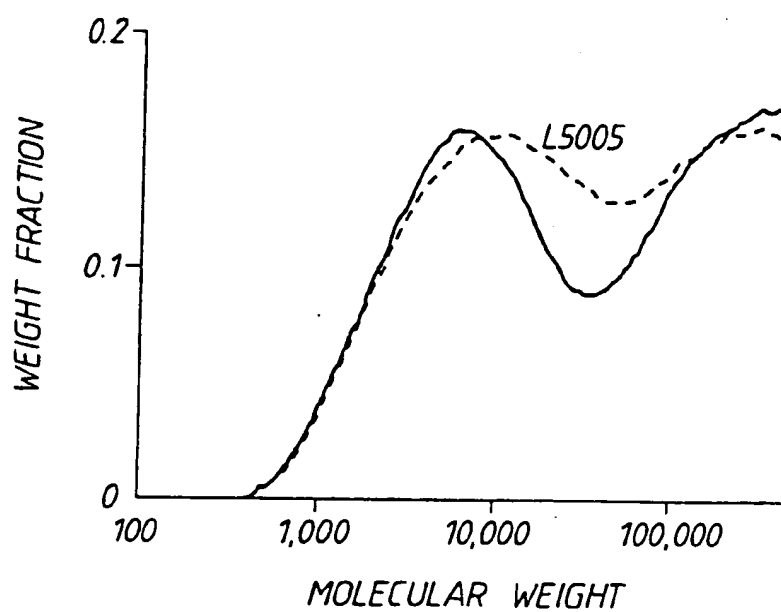
Fig.1

2/3

Fig.2

Fig.3

Fig.4

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08F 4/646
US CL :502/104,107,113,115,117,120; 526/114,116,160

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104,107,113,115,117,120; 526/114,116,160

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,536,484 (Lacombe et al.) 20 August 1985, all pages	1-16
A	US, A, 4,701,432 (Welborn, Jr.) 20 October 1987, all pages	1-16
A	US, A, 4,874,734 (Kloka et al.) 17 October 1989, all pages	1-16
A	US, A, 4,937,301 (Chang) 26 June 1990, all pages	1-16
A	US, A, 4,937,217 (Chang) 26 June 1990, all pages	1-16
A	US, A, 5,026,797 (Takahashi) 25 June 1991, all pages	1-16

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O"	document referring to an oral disclosure, use, exhibition or other means	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 February 1994	14 MAR 1994

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ASOK PAL
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-3809

Form PCT/ISA/210 (second sheet)(July 1992)*

I.   ational application No.

PCT/US93/12084

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,032,562 (Lo et al.) 16 July 1991, all pages	1-16
A	US, A, 5,077,255 (Welborn, Jr.) 31 December 1991, all pages	1-16